2013

Fabrication of graphene electrodes by electrophoretic deposition and their synergistic effects with PEDOT and platinum

Widsanusan Chartarrayawadee
University of Phayao, wc447@uow.edu.au

Simon E. Moulton
University of Wollongong, smoulton@uow.edu.au

Chee O. Too
University of Wollongong, chee@uow.edu.au

Gordon G. Wallace
University of Wollongong, gwallace@uow.edu.au

Publication Details

Chartarrayawadee, W., Moulton, S. E., Too, C. O. & Wallace, G. G. (2013). Fabrication of graphene electrodes by electrophoretic deposition and their synergistic effects with PEDOT and platinum. Chiang Mai Journal of Science, 40 (4), 750-762.

Fabrication of graphene electrodes by electrophoretic deposition and their synergistic effects with PEDOT and platinum

Abstract
This research presents a useful electrophoretic deposition (EPD) technique for electrode fabrication from an aqueous colloidal solution of graphene to produce graphene electrodes by the deposition of graphene on to indium-tin oxide (ITO) coated glass. Resultant graphene electrodes are composited with conducting polymer (PEDOT), and platinum nanoparticles, to investigate their synergistic effects. Firstly, PEDOT is composited with graphene by electropolymerization on to the graphene layer. The graphene/PEDOT electrodes demonstrate an improvement in electrochemical response in tetrabutylammonium perchlorate/ acetonitrile solution. Secondly, graphene electrodes are composited with platinum by EPD of platinum nanoparticles on to the graphene layer. The resultant graphene/platinum electrodes show evidence of an encouragement of the deposition of platinum particles on to the graphene layer, and also show an electro-catalytic activity in the I-/I3 - redox system with an increase in electrochemical response with increasing platinum loading. These graphene composite electrodes show potential for applications in electrochromics (graphene/PEDOT electrodes), and dye-sensitized solar cells (DSSC) (graphene/Pt electrodes).

Keywords
pedot, platinum, synergistic, their, effects, deposition, fabrication, electrophoretic, electrodes, graphene

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details
Chartarrayawadee, W., Moulton, S. E., Too, C. O. & Wallace, G. G. (2013). Fabrication of graphene electrodes by electrophoretic deposition and their synergistic effects with PEDOT and platinum. Chiang Mai Journal of Science, 40 (4), 750-762.

Chiang Mai J. Sci. 2013; 40(4) : 750-762
http://it.science.cmu.ac.th/ejournal/
Contributed paper

Fabrication of Graphene Electrodes by Electrophoretic Deposition and Their Synergistic Effects with PEDOT and Platinum

Widsanusan Chartarrayawadee*[a], Simon E. Moulton [b], Chee O. Too [b] and Gordon G. Wallace*[b]

[a] Department of Chemistry, School of Science, University of Phayao, Phayao 56000, Thailand.
[b] ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, New South Wales 2522, Australia.
*Author for correspondence; e-mail: widsanusan.ch@up.ac.th; gwallace@uow.edu.au

Received: 27 September 2012
Accepted: 9 April 2013

ABSTRACT

This research presents a useful electrophoretic deposition (EPD) technique for electrode fabrication from an aqueous colloidal solution of graphene to produce graphene electrodes by the deposition of graphene on to indium-tin oxide (ITO) coated glass. Resultant graphene electrodes are composited with conducting polymer (PEDOT), and platinum nanoparticles, to investigate their synergistic effects. Firstly, PEDOT is composited with graphene by electropolymerization on to the graphene layer. The graphene/PEDOT electrodes demonstrate an improvement in electrochemical response in tetrabutylammonium perchlorate/ acetonitrile solution. Secondly, graphene electrodes are composited with platinum by EPD of platinum nanoparticles on to the graphene layer. The resultant graphene/platinum electrodes show evidence of an encouragement of the deposition of platinum particles on to the graphene layer, and also show an electro-catalytic activity in the I^-/I_3^- redox system with an increase in electrochemical response with increasing platinum loading. These graphene composite electrodes show potential for applications in electrochromics (graphene/PEDOT electrodes), and dye-sensitized solar cells (DSSC) (graphene/Pt electrodes).

Keywords: graphene, electrophoretic deposition, platinum, PEDOT

1. INTRODUCTION

Graphene is a new kind of carbon material which has a structure composed of one-atom-thick planar sheets of carbon with sp^2 hybridization that are packed densely in a benzene ring structure or honeycomb lattice [1]. Graphene has many outstanding properties such as electron transport, mechanical properties, and high surface area [2, 3]. Furthermore, graphene is easily synthesized [4, 5] at low production cost. Nowadays, composite materials of graphene with other materials, such as metals and polymers, enjoy a tremendous increase in interest [6-8] because graphene plays a

significant role in improving physical and electrochemical properties when working synergistically with other materials [2, 7].

Electrophoretic deposition (EPD) is a term for a coating process using the migration of charged colloidal particles under the influence of an electric field (electrophoresis) to deposit onto a polarized electrode [9]. EPD is a very facile technique that can be used on a lab-scale or industry-scale because various materials can be applied with EPD such as polymers, metals, dyes or ceramics. Furthermore, it can be used both in aqueous and non-aqueous media and also on non-conducting substrates [10]. However, care is needed for aqueous EPD due to the electrolysis of water that can cause damage to the fabricated film. There are reports on EPD for use in many applications such as electronic devices [11], solid oxide fuel cell [12] and field emission devices [13].

In this experiment, graphene was prepared by two-step synthesis. Firstly, graphene oxide (GO) was synthesized from graphite oxide by an exfoliation method to obtain a GO colloidal solution. Secondly, the GO colloidal solution was chemically converted to graphene by chemical reduction [14] to yield graphene colloidal solution; making them amenable for electrode fabrication by EPD in this experiment. To fabricate composite electrodes of graphene/PEDOT, electropolymerization of 3,4-ethylenedioxythiophene (EDOT) was used to deposit a Poly (3,4-ethylenedioxythiophene) (PEDOT) layer on an EPD graphene layer, whereas graphene/platinum electrodes were fabricated by anodic EPD of graphene and platinum nanoparticles [10] sequentially so as to produce alternating layers of graphene and platinum nanoparticles. Furthermore, all electrodes were characterized to observe any synergistic effects of graphene with PEDOT or platinum for an improvement in electrochemical response.

2. MATERIALS AND METHODS

Natural graphite (SP-1, Bay Carbon) was purchased from Cabot. Tetrabutylammonium perchlorate (TBAP), lithium iodide, ammonia solution, hydrazine (35 wt% in water), N, N dimethylformamide, sodium nitrate, potassium permanganate, and chloroplatinic acid (8 wt% in water) were obtained from Sigma-Aldrich. Ethylene glycol was purchased from Unilab, APS. Acetone was received from Chem-supply. Acetonitrile and sulphuric acid were supplied by Scharlau. Iodine was obtained from Merck. All chemicals were used as received. Indium-tin-oxide (ITO) coated glass (Rs = 4-8 Ω) was purchased from Delta Technologies Limited (Stillwater, Minnesota, USA), and cut into 1 cm × 2.5 cm pieces. All ITO specimens were washed with detergent, rinsed with water for a few times then acetone, and purged with nitrogen gas prior to use.

Graphene colloidal solution was synthesized by a published method (refer to previous publication by Li D. et al. [14]) except the dialysis step was replaced by a washing step until the pH reached 7. Platinum nanoparticles were synthesized from Chloroplatinic acid (8 wt% in water) by mixing 1.0 mL of Chloroplatinic acid with 50.0 mL ethylene glycol and subjecting the mixture to microwave irradiation at 1200 W for 30 s. Then washed and re-dispersed in acetone by sonication at amplitude 45 for 30 mins.

Electropolymerization of EDOT was carried out using a 3-electrode cell system. Tetrabutylammonium perchlorate (TBAP) (0.1 M) in acetonitrile was used as an electrolyte solution. The applied electropolymerization potential was 1 V for 5 s to avoid any overpotential of electropolymerization.

Electrophoretic deposition of graphene was carried out at 4 V (optimized condition) with different periods in a 2-electrode cell using a potentiostat (eDAQ) EA 160 electrochemical system. Electrophoretic deposition of platinum was conducted in a similar fashion to graphene at an optimized condition of 5 V with periods of 10, 20 and 30 s.

The Zeta potential of graphene and platinum nanoparticles, and size of platinum nanoparticles were determined using light scattering (Nano-ZS Zetasizer, Malvern Instruments) with back scatter detection ($\theta = 173°$). Scanning electron microscopy (Jeol JSM-7500F Field Emission Scanning Electron Microscope) was used to study the microstructure of graphene electrodes, graphene/platinum electrodes and graphene/PEDOT electrodes. Transmittance of graphene and graphene composite electrodes was measured using UV-vis spectroscopy (Model Shimadzu UV-1800 spectrophotometer with UVProbe (v.2.10) software).

Cyclic voltammetry (CV) characterization of graphene/PEDOT electrodes in TBAP (0.1 M)/acetonitrile was performed over a potential range of -1.0 to 0.8 V using a graphene/PEDOT working electrode, Pt mesh counter electrode and an Ag/Ag^+ reference electrode at a scan rate of 50 mV s^{-1}. All CVs were performed using a potentiostat (eDAQ) EA 160 electrochemical system.

Electrochemical behavior of graphene/platinum electrodes was studied in I^-/I_3^- by cyclic voltammetry in a three-electrode cell with a graphene/platinum working electrode, Pt mesh counter electrode and an Ag/Ag^+ reference electrode at a scan rate of 50 mV s^{-1}. TBAP (0.1 M), LiI (0.01 M) and I_2 (0.005 M) in acetonitrile was used as an electrolyte solution. The potential window used in this experiment was -0.7 V to 1.0 V.

3. RESULTS AND DISCUSSION

3.1 Electrode Fabrications

As we discussed earlier, the important key of the EPD technique is a movement of charged colloidal particles under the influence of an electric field. Synthesized graphene particles in the colloidal solution for EPD in this experiment should possess charges on them, thus making them amenable for electrode fabrication by EPD. To investigate these charges on the graphene colloidal particles, their zeta potential needs to be determined to ascertain their migration behavior under an electric field. A positive or negative value of zeta potential results in cathodic or anodic movement in EPD respectively. The zeta potential of our graphene colloidal solution was characterized as shown in Figure 1. It can be seen that a zeta potential distribution curve of graphene colloidal solution had a mean value of -38.0 mV. This means that graphene has a negative surface charge and can be moved towards a positively polarized electrode under an electric field. The negative surface charge on the graphene particles resulted from the ionization of carboxylic acid and phenolic hydroxyl groups on graphene oxide sheets that are still present after reduction [14]. Furthermore, these negative surface charges contributed to the stability of the graphene colloidal solution because of electrostatic repulsion between them.

To observe the charged particle movement phenomenon in EPD, graphene colloidal solution was placed in a U-shaped tube and platinum wires were placed in the solution at each side of the tube, after which a 4 V potential was applied. It can be observed that the negatively charged graphene particles migrated to the platinum positive electrode at the right hand side of the U-shaped tube

resulting in the disappearance of black colour at the left side and increased black colour at the right side as shown in Figure 2. This phenomenon demonstrated that the migration of graphene particles under an electric field resulted from the negative charge on the graphene particles' surface and we can identify this process as anodic EPD.

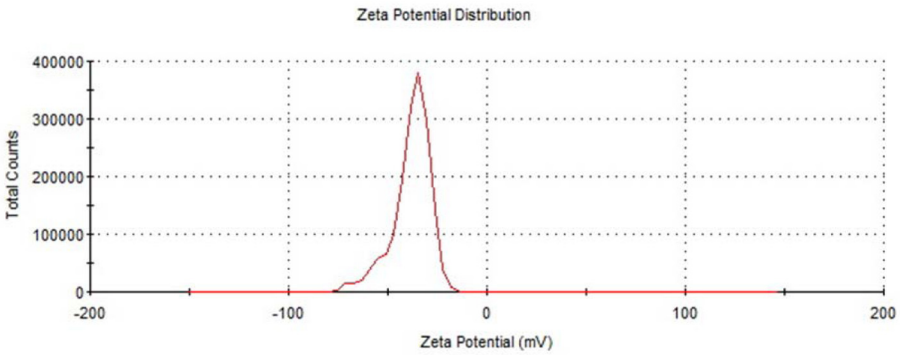

Figure 1. Zeta potential distribution curve of graphene sheets in colloidal solution.

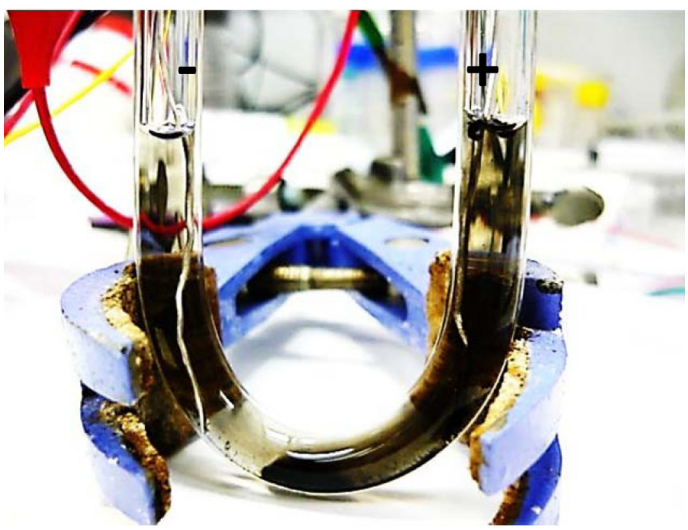

Figure 2. A movement of negatively charged graphene in a colloidal solution (left hand side) to the positively polarized electrode (right hand side)

In preliminary work, graphene was subjected to anodic EPD onto ITO-coated glass under applied potential 4 V (this potential was optimized for graphene colloidal solution in this experiment) for 5 sec (Figure 3) in order to observe the deposition behavior of graphene sheets on ITO-coated glass. SEM images of EPD graphene for 5 sec at 1300x (Figure 4a) shows an uneven network of graphene sheets (black areas) on the ITO layer (white areas). An uneven pattern of graphene coverage resulted from the short EPD period. A short EPD period does not allow enough time for the graphene sheets to deposit on the ITO-coated glass surface to obtain large area coverage which resulted in an uneven graphene pattern. A high magnification SEM image at 37000x in Figure 4b shows that different sizes of fragmented graphene sheets deposited on the ITO layer and overlaid

each other in a stacking manner. It can be observed that graphene prepared by acid oxidation and sonication process resulted in sheet fragmentation. So we cannot expect to prepare equally sized graphene sheets by this method.

When the EPD period was increased, the ITO surface was better covered by the graphene layer as shown in Figure 4c (15 sec deposition). At a deposition period of 30 sec, it can be observed that the ITO layer was almost completely covered by graphene; as shown in Figure 4d where the tiny white areas are ITO and the black areas are graphene. This infers that the EPD period is another key factor for the EPD process to obtain an increasing amount of substance loading on the substrate; where increasing EPD periods resulted in increasing substance loadings. The high magnification SEM image at 50000x of a 30 sec EPD deposition (Figure 4e) illustrates that the deposited graphene sheets overlay each other to obtain good graphene coverage, and we can observe wrinkling of the graphene sheets.

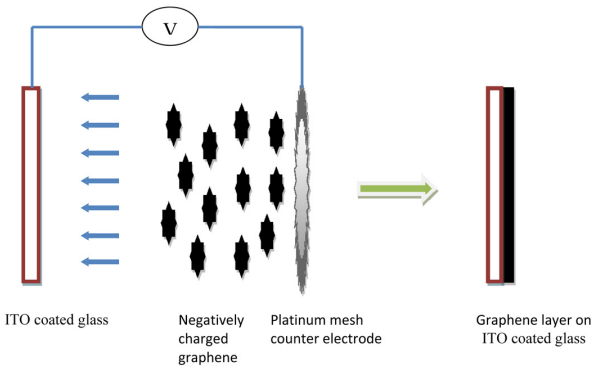

Figure 3. Schematic of electrophoretic deposition of graphene.

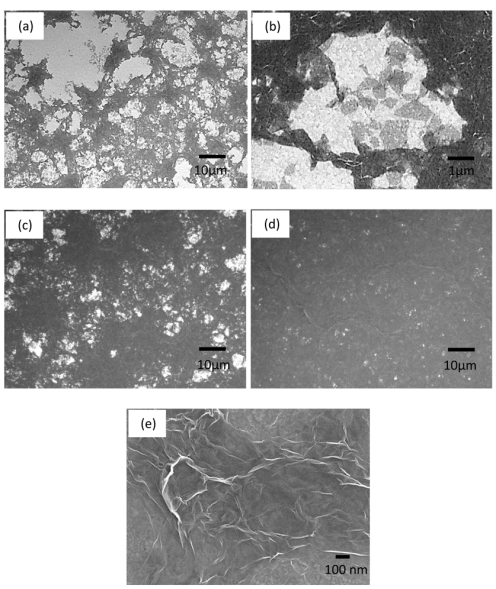

Figure 4. SEM images of graphene sheets deposited on ITO-coated glass by electrophoretic deposition at 4 V (using a 2 electrode-cell) for: (a) 5 sec (SEM at 1300x), (b) 5 sec (SEM at 37000x), (c) 15 sec (SEM at 1300x), (d) 30 sec (SEM at 1300x), and (e) 30 sec (SEM at 50000x).

In this experiment, there are 2 rationales for depositing graphene on the conductive ITO layer. Firstly, we expected to increase the electrochemically active surface area of the electrode over and above that of the ITO electrode alone. Secondly, we expected the graphene layer to promote electrochemical response, and encourage the deposition of other particles on to the graphene layer. However, another additional interesting and important property of graphene is its transparency. Single graphene sheet absorbs 2.3% of incident white light [15] and graphene, moreover, has good electrical property as well. So a combination of these properties makes graphene an outstanding candidate as a transparent conductive electrode for some applications such as in DSSC and electrochromics. The transmittance of fabricated graphene electrodes was measured at 565 nm as shown in Figure 5. The transmittance was found to be decreased when the EPD deposition period of graphene was increased, as expected because of the deposition of graphene sheets on ITO coated glass layer. The transmittance of graphene electrodes of EPD period 5 sec shows a transmittance of up to 85 percent that decreased to around 65 percent after 30 sec deposition (ITO layer not included). This suggests that solution processing of graphene and the EPD technique are compatible and can be used as a material and method respectively to fabricate graphene coated electrodes that can be used as semi-transparent electrodes in some technology applications such as photovoltaic devices/solar cells, Field Effect Transistor (FET) applications, and photodetectors where optical transparency is required.

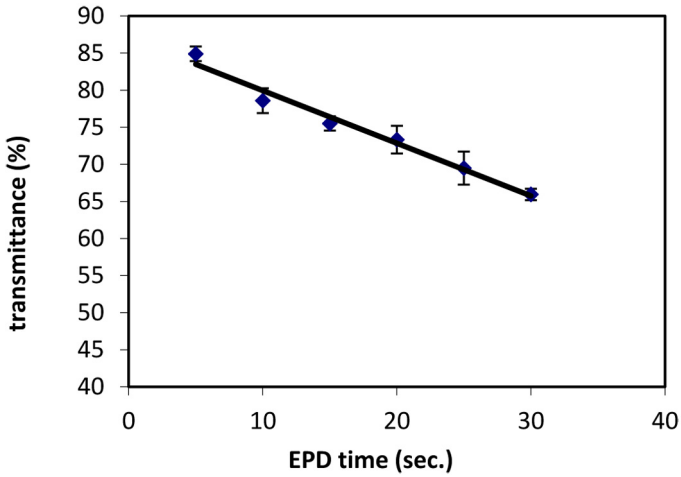

Figure 5. The transmittance of graphene deposited on substrates by electrophoretic deposition (EPD).

3.2 Synergy with PEDOT

In this section, graphene electrodes were composited with conducting polymer, PEDOT, to observe any effect of graphene on an improvement of electrochemical response of PEDOT. EDOT monomer was electropolymerized on a graphene coated electrode at 1 V for 5 sec; to prevent the degradation of polymer that can occur at high overpotentials and long electropolymerization periods. Therefore when the electropolymerization was accomplished, it can be observed from Figure 6 that the deposit of PEDOT on the substrate had a grass-like structure that fully covered the

graphene surface, although the polymerization period was only a short time (5 seconds). This is an advantage in electrochromic applications because optical transmittance of the electrode is an important factor to obtain good optical contrast. So, the transmittance of the graphene/PEDOT electrodes produced over a short electropolymerization period would be higher and the electrodes also afford higher optical contrast. In other words, if the growth of PEDOT film is much thicker, lower optical transmittance and optical contrast would be observed; which are drawbacks for electrochromic applications. In this investigation, the transmittance of graphene/PEDOT electrodes was measured at 565 nm and found that the transmittance of graphene/PEDOT electrodes at EPD graphene for 5 sec gave the highest transmittance which is almost up to 80 percent as shown in Figure 7. However, transmittance decreased with increasing graphene EPD period as expected and EPD graphene at 30 sec reduced the transmittance to approximately 55 percent, which could be undesirable for electrochromics.

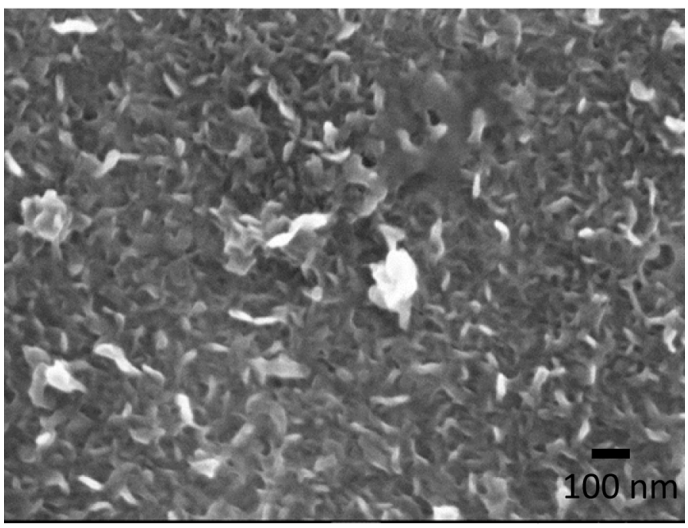

Figure 6. SEM image at 85000x of electropolymerized PEDOT on graphene.

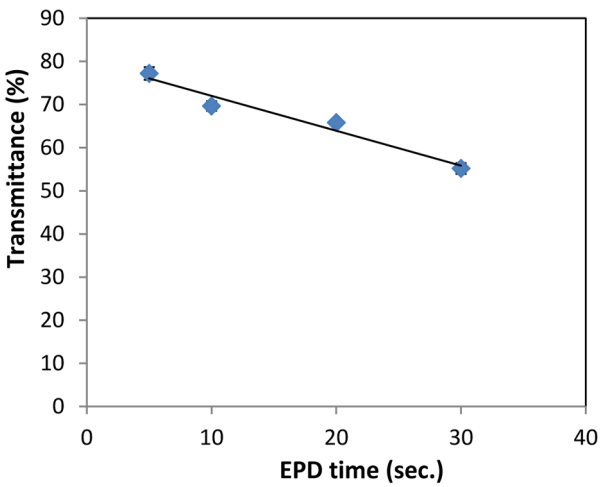

Figure 7. The transmittance of graphene/PEDOT electrodes.

To investigate the electrochemical behavior of graphene/PEDOT composite electrodes, cyclic voltammograms (Figure 8) of graphene/PEDOT electrodes were scanned over a wide potential window of -1.0 V to 0.8 V (vs Ag/Ag^+) in 0.1 M tetrabutylammonium perchlorate (TBAP)/ acetonitrile at 50 mV s^{-1}. It can be observed that PEDOT and graphene/PEDOT electrodes show an oxidation peak at around -0.16 V and a reduction peak at around -0.8 V. Changes in oxidation and reduction states of PEDOT and graphene/PEDOT electrodes over this potential range indicated that these electrodes have potential for use in electrochromic applications due to their concomitant colour switching. The colour switched from reduced state (darkened) to oxidized state (bleached) and vice versa. Furthermore, it can be observed that the current increased with increasing graphene deposition period. This can be attributed to thicker layers of graphene which increase the conductivity and electrochemical surface area that resulted in a larger area of electrodeposited PEDOT. However, there was the slight shift in the reduction peaks of graphene/PEDOT electrodes to more negative potentials resulting in wider peak separations. This can be explained by the EPD graphene layer having a lower conductivity than ITO layer which contributed to the slower electron transfer.

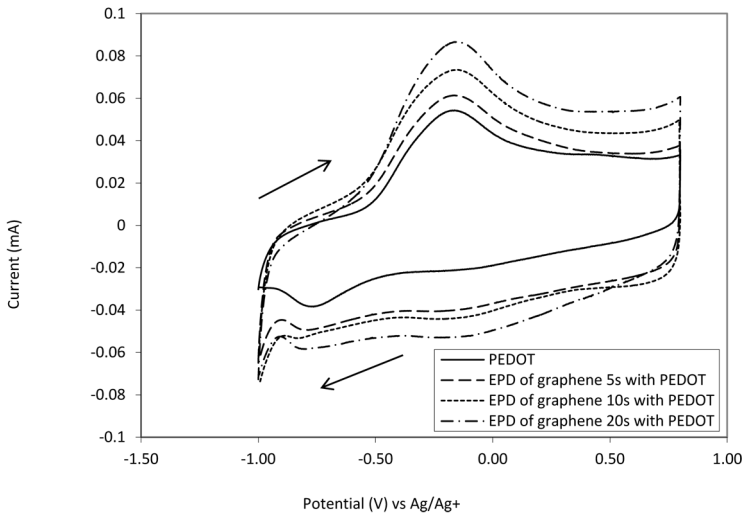

Figure 8. CVs of graphene/PEDOT electrodes in 0.1 M TBAP/ acetonitrile at 50 mV s^{-1} for different graphene deposition periods. PEDOT was grown for 5 sec at 1.0 V.

3.3 Synergy with platinum

In this section, graphene electrodes were composited with platinum nanoparticles, by sequential EPD layering of graphene and platinum respectively, to observe their catalytic property for potential uses in dye-sensitized solar cells. In preliminary work, platinum nanoparticles were characterized by measuring their size and zeta potential for performing EPD. From Figure 9a and 9b, it can be seen that the average size of platinum nanoparticles was around 300 nm and the zeta potential was -12.6 mV. This indicates that the solution is of incipient stability (higher value of zeta potential (negative or positive) results in better colloidal stability); which means that although the solution in not stable in the long term, it is stable while performing EPD. Due to the negative zeta potential of the platinum nanoparticles, we expected that anodic EPD

of platinum can be achieved on a graphene layer similar to anodic EPD of graphene on ITO coated glass.

To observe the behaviour of the deposition of platinum on graphene and improvement of electrochemical response with platinum loading, platinum nanoparticles were deposited on a graphene layer by anodic EPD. In this experiment, graphene was EPD on ITO for 30 sec to obtain a good graphene coverage. Following this, platinum was EPD on to graphene for 10, 20 and 30 sec to observe their deposition pattern on the graphene layer. From the SEM images in Figures 10a to 10f, it can be observed that the loading of platinum deposited on the graphene layer increased when the EPD period was increased. At low EPD period (10 and 20 sec), the deposition of platinum nanoparticles on the graphene layer is heterogeneous. However, when the EPD period was increased to 30 sec a homogeneous distribution of platinum nanoparticles can be observed. Another interesting phenomenon was observed in that the size of platinum nanoparticles deposited on graphene is approximately 100-120 nm, from which it can be deduced that the smaller sized platinum particles chose to deposit on the graphene layer. The reasons are that the smaller size particles can carry more charge and are of lower mass, thus facilitating migration under the influence of an electric field in EPD; while large size particles tend to precipitate. This explanation is supported by the size distribution profile of the platinum solution in Figure 9a which demonstrates that the smallest size of platinum nanoparticles were approximately 100 nm. Furthermore, the SEM image (Figure 10g) shows that platinum nanoparticles (white particles) preferred to deposit on graphene (black areas) than on ITO glass (grey areas). In addition, a greater amount of graphene deposited on the ITO glass leads to more platinum particles deposited on the graphene. This result demonstrated that graphene assists the deposition of platinum nanoparticles in this system.

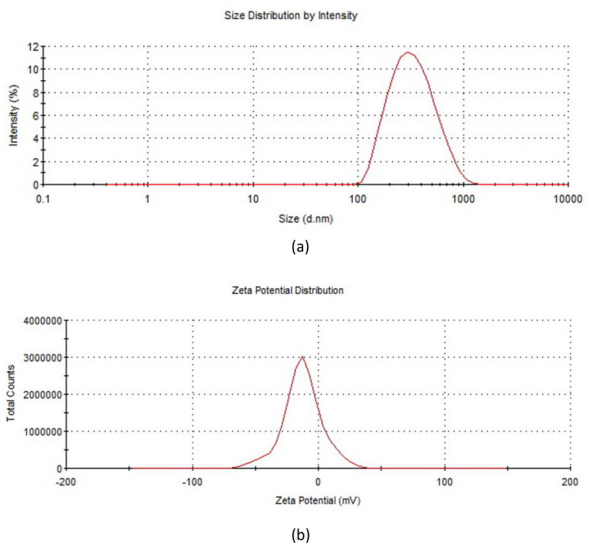

Figure 9. Size distribution curve (a) and zeta potential distribution curve (b) of platinum nanoparticles in acetone.

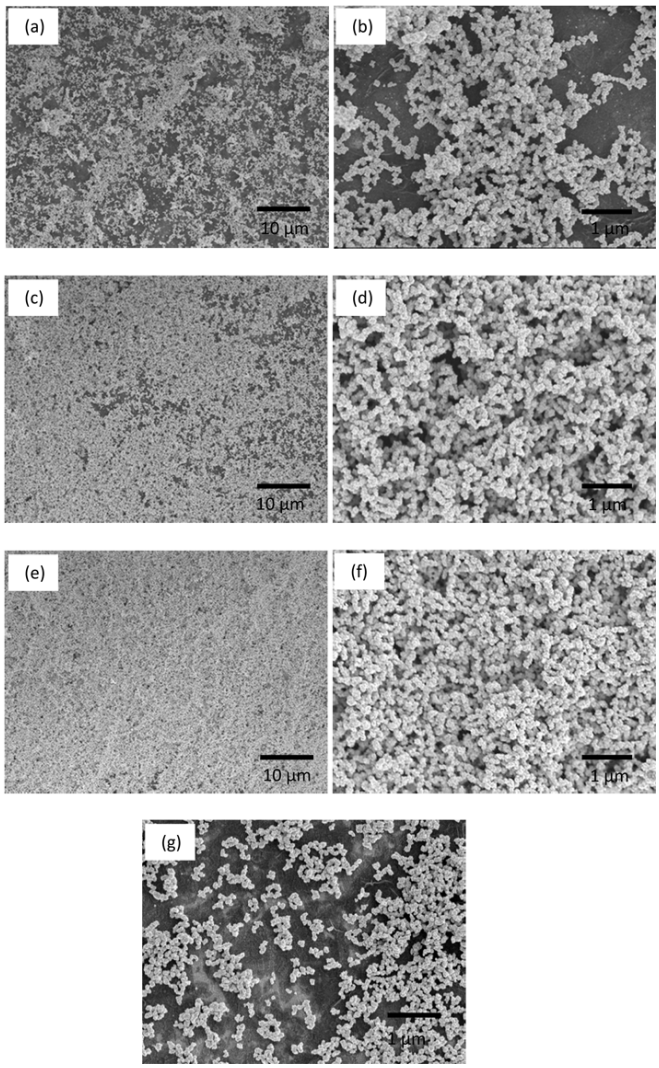

Figure 10. SEM images of platinum nanoparticles deposited on EPD graphene by electrophoretic deposition at 5 V (using a 2 electrode-cell) for: (a) 10 sec (SEM at 2000x), (b) 10 sec (SEM at 20000x), (c) 20 sec (SEM at 2000x), (d) 20 sec (SEM at 20000x), (e) 30 sec (SEM at 2000x), (f) 30 sec (SEM at 20000x). (g) SEM image showing that platinum preferred to deposit on graphene than on ITO.

To investigate the electrochemical behavior of the graphene/platinum composite electrodes, they were then characterized in the iodide/triiodide system to ascertain their potential properties that could be useful for dye-sensitized solar cells; e.g. as counter electrodes. The cyclic voltammograms (Figure 11) of the iodide/triiodide system obtained at graphene/platinum electrodes were scanned over a wide potential window from -0.7 V to 1 V vs Ag/Ag^+ in 0.1 M tetrabutyl ammonium perchlorate (TBAP), 0.01 M LiI, 0.005 M I_2 in ACN at 50 mV s^{-1}. It can be seen that two redox couples were detected at the graphene/platinum electrode but not two at the graphene electrode. The graphene electrode induced redox of the I_3^-/I_2 couple but only oxidation of I^- to I_3^-

(0.4 V); demonstrating that the I^-/I_3^- couple was irreversible at the bare graphene electrode. Therefore, the graphene/platinum electrode is superior to the graphene electrode as a catalytic electrode in this electrolyte system. The redox equations are given below [16]:

$I_3^- + 2e^- \rightarrow 3I^-$ (-0.26 / +0.14 at graphene/Pt electrode in Figure 11)

$3I_2 + 2e^- \rightarrow 2I_3^-$ (+0.33 / +0.62 at graphene/Pt electrode Figure 11)

It can also be seen that a higher loading of platinum on the graphene electrode resulted in a higher redox activity towards I_3^- and I_2 as we can observe that the current increased with EPD period of platinum nanoparticles. This suggests their potential to be used in a solar cell as a counter electrode [17, 18].

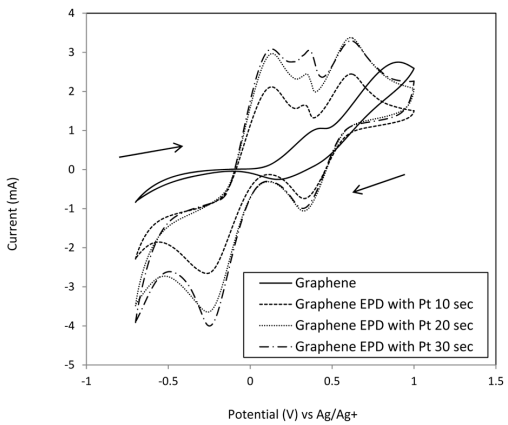

Figure 11. CVs obtained at graphene/Pt electrodes, with different loading of Pt, in 0.01 M LiI, 0.005 M I_2, 0.01 M TBAP in acetonitrile at 50 mV s^{-1} compared with a graphene electrode.

3.4 Potential application in the future

In preliminary work, we tried to electrophoretically deposit graphene on Poly(N-isopropylacrylamide) gel as shown in Figure 12 to produce a conductive layer of graphene on temperature-responsive hydrogel which could be used in applications that need a conducting gel with phase transition. This can open up the avenue of using the EPD technique to fabricate graphene electrode not just only on solid substrates but also on a flexible substrate as well.

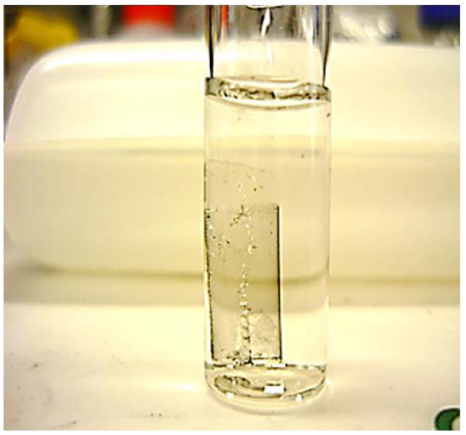

Figure 12. Electrophoretic deposition of graphene layer on temperature-responsive Poly(N-isopropylacrylamide) hydrogel.

4. CONCLUSION

In conclusion, we fabricated graphene and graphene composite electrodes by electrophoretic deposition. Graphene electrodes show potential to be used as a semi-transparent electrode in some technology applications where optical transparency is required. For graphene/PEDOT composite electrodes, graphene promotes electrochemical responses resulting in higher peak current in cyclic voltammograms as a function of graphene deposition period. This can be explained by an enhancement in the electrochemical surface area that resulted in a larger area of electrodeposited PEDOT. The concomitant colour change of PEDOT with the electrochemical redox of this polymer shows promise for graphene/PEDOT electrodes to be used in electrochromic applications. In further experiments, graphene is shown to attract platinum nanoparticles deposition in the studied EPD system. The graphene/platinum composite electrodes produced also show promise as catalytic electrode materials for use in a solar cell as a counter electrode.

ACKNOWLEDGEMENTS

Financial support from the Australian Research Council is gratefully acknowledged by the co-authors affiliated with the ARC Centre of Excellence for Electromaterials Science. The Phayao University is gratefully acknowledged for their support.

REFERENCES

[1] Geim A. K. and Novoselov K. S., The rise of graphene, *Nat. Mater.,* 2007; **6:** 183-191.

[2] Stoller M. D., Park S. Zhu Y., An J. and Ruoff R. S., Graphene-based ultracapacitors, *Nano Lett.,* 2008; **8:** 3498-3502.

[3] Bolotin K. I., Ultrahigh electron mobility in suspended graphene, *Solid State Commun.,* 2008; **146:** 351-355.

[4] Wang G., Yang J., Park J., Gou X., Wang B., Liu H. and Yao J., Facile synthesis and characterization of graphene nanosheets, *J. Phys. Chem., C: Nanomater. Interfaces,* 2008; **112:** 8192-8195.

[5] Shan C., Tang H., Wong T., He L. and Lee S.-T., Facile synthesis of a large quantity of graphene by chemical vapor deposition: An advanced catalyst carrier, *Adv. Mater.,* 2012; **24:** 2491-2495.

[6] Yen M.-Y., Teng C.-C., Hsiao M.-C., Liu P.-I., Chuang W.-P., Ma C.-C. M., Hsieh C.-K., Tsai M.-C. and Tsai C.-H., Platinum nanoparticles/graphene composite catalyst as a novel composite counter electrode for high performance dye-sensitized solar cells, *J. Mater. Chem.,* 2011; **21:** 12880-12888.

[7] Kim H., Abdala A. A. and Macosko C. W.,Graphene/polymer nanocomposites, *Macromolecules,* 2010; **43:** 6515-6530.

[8] Wu Z.-S., Zhou G., Yin L.-C., Ren W., Li F. and Cheng H.-M., Graphene/metal oxide composite electrode materials for energy storage, *Nano Energy,* 2012; **1(1):** 107-131.

[9] Besra L. and Liu M., A review on fundamentals and applications of electrophoretic deposition (EPD), *Prog. Mater. Sci.,* 2007; **52:** 1-61.

[10] Besra L., Compson C. and Liu M., Electrophoretic deposition on non-conducting substrates: The case of YSZ film on NiO-YSZ composite substrates for solid oxide fuel cell application, *J. Power Sources,* 2007; **173:** 130-136.

[11] van Tassel J. and Randall C. A., Potential for integration of electrophoretic deposition into electronic device manufacture; demonstrations using silver/palladium, *J. Mater. Sci.,* 2004; **39:** 867-879.

[12] Zhitomirsky I. and Petric A., Electrophoretic deposition of electrolyte materials for solid oxide fuel cells, *J. Mater. Sci.,* 2004; **39:** 825-831.

[13] Zhong-Shuai W., Songfeng P., Wencai R., Daiming T., Libo G., Bilu L., Feng L., Chang L. and Hui-Ming C., Field emission of single-layer graphene films prepared by electrophoretic deposition, *Adv. Mater.,* 2009; **21:** 1756-1760.

[14] Li D., Muller M. B., Gilje S., Kaner R. B. and Wallace G. G., Processable aqueous dispersions of graphene nanosheets, *Nat. Nanotechnol.,* 2008; **3:** 101-105.

[15] Nair R. R., Blake P., Grigorenko A. N., Novoselov K. S., Booth T. J., Stauber T., Peres N. M. R. and Geim A. K., Fine structure constant defines visual transparency of graphene, *Science,* 2008; **320:** 1308.

[16] Chartarrayawadee W., Moulton S. E., Li D., Too C. O. and Wallace G. G. Novel composite graphene/platinum electro-catalytic electrodes prepared by electrophoretic deposition from colloidal

solution, *Electrochim. Acta.,* 2012; **60:** 213-223.

[17] Li P., Wu J., Lin J., Huang M., Huang Y. and Li Q., High-performance and low platinum loading Pt/Carbon black counter electrode for dye-sensitized solar cells, *Solar Energy,* 2009; **83:** 845-849.

[18] Huang Z., Liu X., Li K., Li D., Luo Y., Li H., Song W., Chen L. and Meng Q., Application of carbon materials as counter electrodes of dye-sensitized solar cells, *Electrochem. Commun.,* 2007; **9:** 596-598.